

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.3:536.246

CORRELATION OF AQUEOUS-PHYSICAL, STRUCTURAL-MECHANICAL, AND THERMOPHYSICAL PROPERTIES OF MOIST DISPERSE MATERIALS

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It is shown that the cohesiveness and plastic strength of moist materials and their thermophysical and drying properties are determined by the ratio of capillary-mobile and capillary-immobile moisture forms and natural properties of materials which can be best estimated based on the least capillary moisture or the maximum molecular moisture capacity which are the most significant aqueous-physical parameters of materials. Formulas are proposed for the calculation of the dependence of cohesiveness and plastic strength of materials on their moisture content and drying sensitivity, as well as formulas for the calculation of thermophysical properties of moist materials.

Among the great variety of disperse systems used in ceramic technologies, the most common are systems in which the liquid phase is represented by water. The physicochemical and physicomachanical properties of these systems are determined by the amount and properties of water contained in them, which enters in a complex interaction with the solid phase particle surface, which interaction is determined by the structural specifics of water, the high polarity of water molecules, the presence of the hydrogen bond between them, and the anomaly of water properties. The capability of solid bodies for physicochemical reactions with water is determined by the properties of these bodies: chemical and mineral composition, the type of crystal lattice, dispersion, surface state, and other factors. The mutual adhesion force of solid phase particles depends on the energy of reaction between the boundary water and solid phase molecules and, accordingly, on the thickness of the liquid interlayer between the particles, which determines the structural-mechanical and the rheological properties of the disperse system.

Analysis of contemporary concepts of the forms of bond between moisture and material and classification of types of moisture suggests that in solving technological problems, it is convenient to distinguish physicochemically and physicomachanically bound water as two main categories (Fig. 1): capillary-mobile moisture (CMM) and capillary-immobile moisture (CIM). A specific feature of CMM is its capacity to transmit hydrostatic pressure and migrate in the form of liquid within the structure of the material. CIM does not trans-

mit hydrostatic pressure and can be removed from material only in the form of vapor. An arbitrary boundary between these moisture categories is the least capillary moisture W_{LCM} , i.e., the least moisture content under which the molecules of adsorbed or film water are retained by microcapillaries inside the pore space of solid phase particles compacted to the maximum extent. According to A. F. Lebedev and A. M. Vasil'ev [1, 2], the least capillary moisture correlates with the maximum molecular moisture capacity of material W_{MMC} . Researchers believed that this moisture is retained only by molecular forces, and therefore, dispute the existence of W_{MMC} as a separate moisture category [3]. That is why in the terminological and conceptual context it is best to designate the capillary-immobile moisture as "the least capillary moisture."

The CIM of a disperse system can be determined using the method of moisture-retaining media, the centrifuging

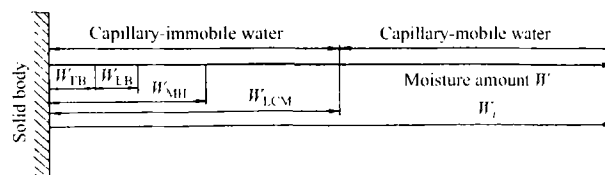


Fig. 1. Scheme of retention of various forms of moisture by a solid particle surface: W_{FB}) firmly bound water; W_{LB}) loosely bound water; W_{MH}) maximum hygroscopic moisture; W_{LCM}) the least capillary moisture; W_i) the current value of material moisture.

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method [1, 2], and the method of capillary impregnation of a dry layer of material under varying packing density [4, 5]. According to the latter method, dry finely disperse material is placed in glass tubes 1 – 1.5 cm in diameter and 5 – 7 cm high with a porous bottom, then compacted and brought into contact with water. The kinetics of capillary impregnation is evaluated from the impregnated layer height or the adsorbed water volume and the impregnation duration, for which purpose a graduating scale of millimeter-graduated paper is glued to the lateral surface of the tube. The height of the impregnated layer should be at least 3 – 5 cm. The speed of moisture migration inside the material layer is estimated from the capillary impregnation coefficient (cm^2/sec):

$$K_{CI} = \frac{h^2}{\tau} = \frac{V^2}{(SP)^2} \tau,$$

where h is the impregnated layer height, cm; τ is the impregnation duration, sec; V is the adsorbed water volume, cm^3 ; S is the cross-lateral surface of the impregnated layer, cm^2 ; P is the porosity of the layer; $P = 1 - K_s$, $K_s = \rho_{ap}/\rho_t$ (ρ_{ap} is the apparent density of the layer, kg/m^3 , ρ_t is the true density of the layer, kg/m^3).

If the material does not dissolve or swell in water, the relationship between K_{CI} , the moisture content of the layer W , and the volume concentration of the solid phase K_s are linear (Fig. 2). Extrapolation of the straight line $W = f(K_{CI})$ to the intersection with the moisture content axis ($K_{CI} = 0$) produces a segment whose size correlates with W_{LCM} . Extrapolation of the straight line $K_s = f(K_{CI})$ to the intersection with the axis K_s produces a segment characterizing the maximum possible packing of the material layer, under which migration of liquid via the material structure will be impossible ($K_{CI} = 0$). The moisture content correlating with such packing of the particle layer, when in the course of capillary saturation the material does not shrink along the tube height, is taken as the maximum capillary moisture or moisture capacity W_{MCM} . The difference $W_{MCM} - W_{LCM}$ represents the maximum amount of CMM which can be retained by the given material. The capacity of disperse materials for retaining various quantities of CMM and CIM depends on the aqueous-physical properties of the material, i.e., on the properties determined by the nature, dispersion, granulometric composition, and volume concentration of the solid phase in the disperse system. Simultaneous solution of the linear equations $W = f(K_{CI})$ and $K_s = f(K_{CI})$ also gives a linear correlation:

$$K_s = -aW + b, \quad (1)$$

where a and b are coefficients which are constant for the particular material.

This relationship is strictly individual for each specific material and reflects the effect of the degree of packing of the solid phase particles on the content of CMM in the interval between W_{MCM} and W_{LCM} . Furthermore, it shows the principal relationship between the aqueous-physical and the struc-

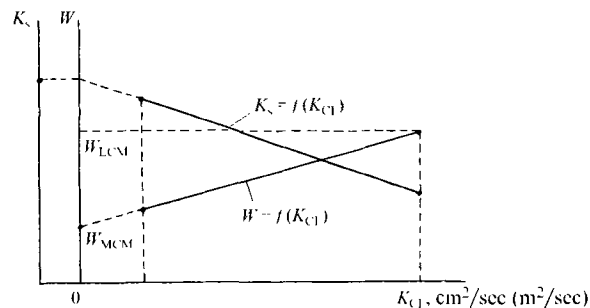


Fig. 2. Dependence of the final moist content W and the capillary impregnation coefficient K_{CI} on the degree of packing K_s of the layer of the material.

tural-mechanical properties of a moist material existing in the two-phase ($S + L$) state. Under the moisture content W_{LCM} , the material has the maximum density and maximum mechanical strength due to the minimum possible thickness of the aqueous interlayer between the particles. The least capillary moisture is the nodal point in the quantitative and qualitative modifications of moist material properties, at which point the main role in retaining water passes from the sorption forces to the capillary forces. An increase in the CMM content in the material ($W_i - W_{LCM}$) increases the thickness of the water interlayers, decreases the value of K_s , and, accordingly, decreases the cohesiveness of the material, which can be estimated from the formula

$$C_i = \varepsilon \frac{W_{LCM}}{W_i - W_{LCM}}, \quad (2)$$

where C_i is the moist material cohesiveness, N/cm^2 , or the energy saturation per volume unit of the mixture, J/m^3 ($1 \text{ N}/\text{cm}^2 = 0.01 \text{ J}/\text{cm}^3 = 10^4 \text{ J}/\text{m}^3$); ε is the dimensional proportionality coefficient, N/cm^2 ; W_i is the current value of the absolute moisture content of the material in relative units.

It follows from the formula that the cohesion of the material determined by the simultaneous actions of the molecular and capillary forces is uniquely determined by the ratio of the quantities of capillary-immobile (W_{LCM}) and capillary-mobile ($W_i - W_{LCM}$) water.

The plastic strength, which is one of the most essential structural-mechanical parameters, is a function of the cohesiveness and the current moisture content of the material:

$$P_m = C_i \varepsilon' \frac{1}{W} = \varepsilon' \frac{W_{LCM}}{W_i - W_{LCM}} \frac{1}{W_i}, \quad (3)$$

where P_m is the plastic strength of the material, MPa; ε' is the dimensional coefficient to convert N/cm^2 to MPa; $\varepsilon' = 0.01$.

The resulting expression also characterizes the relationship between the structural-mechanical and aqueous-physical properties of the material. This correlation was verified by studying the relationship $P_m = f(W_i)$ for Rodionovskoe loam

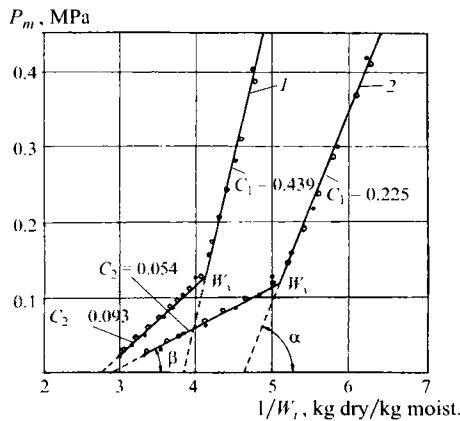


Fig. 3. Dependence of the plastic strength of mixtures P_m on inverse moisture content $1/W_i$: 1) Voronovskoe clay; 2) Rodionovskoe loam; $\circ-\circ-\circ-$ estimated relationship; $-\bullet-\bullet-$ experimental data; $C_1 = \tan \alpha$; $C_2 = \tan \beta$.

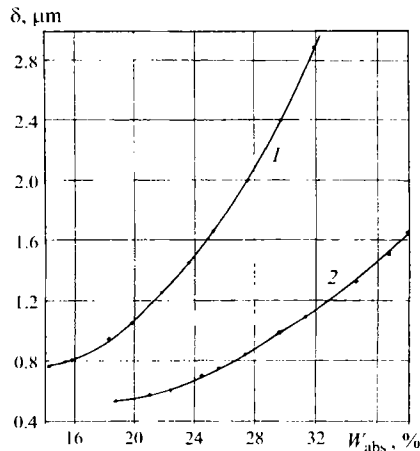


Fig. 4. Dependence of the thickness of interparticle layers δ on absolute moisture W_{abs} of materials: 1) Voronovskoe clay; 2) Rodionovskoe loam.

and Voronovskoe clay (Tomsk Region) using the Rebinder conic plastometer.

In measuring the plastic strength of materials, a modification was introduced to the accepted measuring method [6]: the tested material was placed in a container with a lateral hole 3 mm in diameter and compressed to a state at which the material started to be squeezed out from the hole, i.e., to the critical density for the corresponding moisture content. Preliminary compaction of the material to virtually the two-phase state increases the accuracy of measuring P_m .

In order to obtain the estimated relationship $P_m = f(W_i)$ based on expression (3), the value W_{LCM} was determined using the methods of moisture-retaining media and of capillary impregnation. The absolute discrepancy in the W_{LCM} values determined by two methods does not exceed 1.0–1.5%. The average value of W_{LCM} for Rodionovskoe loam is 14.2%, and for Voronovskoe clay it is 18.7%.

According to expression (3), the obtained results are represented in the coordinates $P_m = f(1/W_i)$ in Fig. 3, from which it follows that this relationship is formed by two rectilinear segments positioned at different angles to the abscissa axis, which characterize the mixture cohesion. With the moisture content W_i , which is related to the intersection point of two straight segments in the relationship $P_m = f(1/W_i)$, the mechanism of structure formation in the material in moistening is altered. With $W_i < W_x$, when the thickness of the water interlayers is insignificant, the cohesion of the mixture is mainly provided by interparticle molecular forces, and with $W_i > W_x$, the effect of the molecular forces significantly decreases, and the capillary forces become predominant.

The ratio of the angle tangents of the upper and the lower rectilinear segments for Rodionovskoe loam is $0.255/0.054 = 4.72$, and for Voronovskoe clay it is $0.439/0.093 = 4.72$. The equality of these two values is evidence of the fact that, regardless of the type of clay, the forces ensuring the coherence of mixtures when $W_i < W_x$ are 4.72 times greater than the forces acting under $W_i > W_x$, and the cohesion of Voronovskoe clay is 1.72 times greater than the cohesion of Rodionovskoe loam ($0.439/0.255 = 0.093/0.054 = 1.72$).

The latter is due to the higher degree of dispersion in Voronovskoe clay ($S_{sp} = 570 \text{ m}^2/\text{kg}$) and the higher content of argillaceous minerals (27.2%), as compared to Rodionovskoe loam ($S_{sp} = 275 \text{ m}^2/\text{kg}$, content of argillaceous minerals 9.0%).

Compression of materials with various levels of initial moisture content to a critical density level or virtually to the two-phase state makes it possible to obtain various structural-phase characteristics: moist material density, apparent density of dry material, relative density of material K_s , porosity $P = 1 - K_s$; based on these values, it is possible to calculate the thickness of the gas-liquid interlayer δ between the particles,

$$\delta = \frac{(1 - K_s) / K_s}{S_f},$$

where S_f is the specific surface area per volume unit of the solid phase, m^2/m^3 ; $S_f = S_m \rho_s$; S_m is the specific surface area per mass unit, m^2/kg ; ρ_s is the apparent density of dry samples, kg/m^3 ; $\rho_s = \rho_m (1 + W_i)$; ρ_m is the moist material density, kg/m^3 ; W_i is the absolute moisture content of the material, relative units.

Figure 4 represents the correlation between the thickness of the interlayers between particles and the absolute moisture content of materials. It can be seen that the thickness of the interlayers, as well as the moisture capacity or water-retaining capacity of the materials, are determined by their dispersion. With W_{LCM} and two-phase (S + L) state of the material, the thickness of liquid interlayers between particles reaches a minimum value, at which the liquid film continuity is preserved throughout the bulk of the material. A decrease in the

moisture content ($W_i < W_{LCM}$) leads to a break in the film continuity and increases the gas phase content in the material, whereas with increasing moisture content ($W_i > W_{LCM}$), capillary-mobile water emerges in the material, the interlayers grow thicker, and the cohesion and plastic strength decrease, and the regularities of these modifications are determined by W_{LCM} of the material. Therefore, W_{LCM} is the key point of the qualitative and quantitative modifications in a moist material and its most significant aqueous-physical parameter, which makes it possible to predict modifications in the structural-mechanical properties of disperse materials in moistening.

The behavior of moist materials in drying is determined by the technological conditions of drying and by the natural properties of materials, which in their integrity can be indirectly estimated using the value of W_{LCM} . Since CMM is capable of migrating inside the material structure in the form of a liquid, its removal, in accordance with equation (1), is accompanied by modifications in the structural-phase parameters and shrinkage of the material. The moisture content under which the shrinkage of the material ceases correlates with W_{MCM} [7, 8]. Taking into account the closeness of the W_{MCM} and W_{LCM} values determined by two different methods, the known formula of Chizhskii [9] for the calculation of drying sensitivity coefficients of materials K_d can be represented in the form

$$K_d = \frac{W_i - W_{LCM}}{W_{LCM}}, \quad (4)$$

where W_i is the molding moisture content of the material, % or relative units; W_{LCM} is the moisture content of the material at the end of drying, % or relative units.

It follows from this formula that the value of K_d depends on the ratio of CMM and CIM quantities, and correlation of formula (2) with formula (4) indicates that the drying sensitivity of moist materials is a value inverse to their cohesiveness:

$$K_d = 1/C_i.$$

The cohesiveness or energy saturation per volume unit of moist material is determined by the level of cohesive-adhesive forces of its structural elements. When the moisture content is close to W_{LCM} , the material has the maximum cohesiveness and the minimum drying sensitivity. The presence of CMM weakens the molecular forces of interparticle interaction and increases the drying sensitivity of the material. Therefore, the content of capillary-mobile moisture and its removal is a most essential factor which determines the structure formation in drying of materials with prescribed geometrical sizes, and according to relationship (1), the rate of removal of CMM ought to correspond to the rate of consolidation or shrinkage of the material.

The aqueous-physical properties of the material, primarily W_{LCM} , determine not only the structural-mechanical pa-

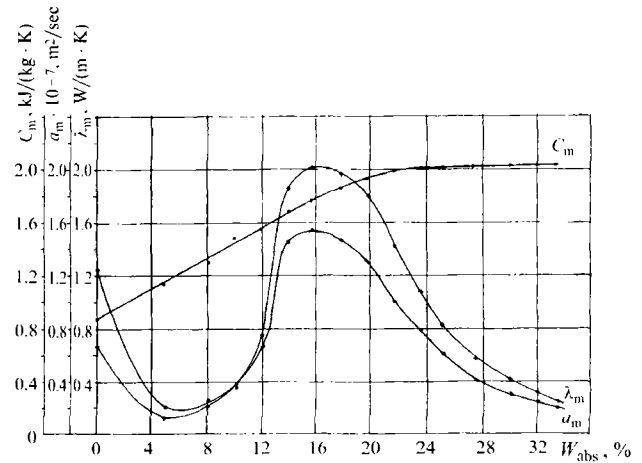


Fig. 5. Dependence of the thermophysical properties of Rodionovskoe loam on absolute moisture.

rameters, but the thermophysical properties of the material as well. An analysis of the known relationships for the calculation of thermophysical properties [10] reveals that they do not take into account the presence of the gas phase. Since heat capacity depends on weight, and weight depends on the volume of the material, a calculation of the heat capacity of a moist material should be carried out taking into account parts by volume, rather than parts by weight, of all phases present:

$$C_m = C_s K_s + C_l K_l + C_g K_g,$$

where C_m is the specific heat of the moist material, kJ/(kg·K); C_s , C_l , and C_g are the specific heats of the solid, liquid, and gas phases; K_s , K_l , and K_g are parts by volume of the solid, liquid, and gas phases.

The gas phase has the highest thermal resistance; therefore, in calculating the thermal conductivity of moist materials, it is also necessary to take into account the ratios and the thermal resistance of the parts by volume of the phases present:

$$\lambda_m = \frac{K_s + K_l}{1 - K_s} \frac{1}{K_s / \lambda_s + K_l / \lambda_l + K_g / \lambda_g},$$

where λ_m is the thermal conductivity of the moist material, W/(m·K); λ_s , λ_l , and λ_g are the thermal conductivities of the solid, liquid, and gas phases.

Based on the known values of C_m , λ_m , and the critical density of the material under a corresponding moisture content ρ_m , it is possible to determine the thermal diffusivity which characterizes the rate of heat expansion:

$$a_m = \lambda_m / (C_m \rho_m).$$

Figure 5 represents the estimated relationship of thermophysical properties of Rodionovskoe loam on absolute moisture. As can be seen, the relationships $\lambda_m = f(W)$ and

$a_m = f(W)$ are extremum, and the maximum values of a_m and λ_m are registered in the interval $W = 14 - 16\%$, i.e., with $W_{LCM} = 14.2\%$, when the layer of adsorbed and film water, which is rigidly oriented by the force field of the particles, becomes continuous throughout the entire bulk of the material. The absence of Brownian movement in this layer and its orderliness facilitate rapid heat expansion inside the moist material.

Voronovskoe clay ($C_{dry} = 0.838 \text{ kJ}/(\text{kg} \cdot \text{K})$, $\lambda_{dry} = 0.73 \text{ W}/(\text{m} \cdot \text{K})$) exhibits a similar dependence of the thermophysical properties on the moisture content. The maximum value of these properties ($\lambda_m = 2.43 \text{ kJ}/(\text{kg} \cdot \text{K})$, $a_m = 1.708 \times 10^{-7} \text{ m}^2/\text{sec}$) also correlates with $W_{LCM} = 18.7\%$. An increase in the CMM content not only increases the drying sensitivity of the material but also degrades its thermophysical parameters, which slows down leads the rate of heating for the material and extends the drying duration.

Thus, the cohesiveness and the structural-mechanical properties of moist materials and their thermophysical and drying properties are determined by the ratio of capillary-mobile and capillary-immobile forms of moisture. The regularities of modifications in this correlation upon variations in the moisture content, in turn, depend on the natural properties of the solid phase, which can be estimated based on the value W_{LCM} , which is the most significant aqueous-physical parameter of a disperse material. The existence of this boundary category of moisture is corroborated not only by the moisture-retaining media method, but by the capillary impregnation method as well. Based on the value W_{LCM} , it is possible to predict the behavior of ceramic mixtures in plastic molding and drying of moist articles with a prescribed geometrical shape.

Studies of a substantial number of materials show that the optimum molding and drying properties are exhibited by

ceramic mixtures which have the least capillary moisture content within the limits of $17 - 22\%$. Within this interval, a mixture successfully combines moisture-retaining and moisture-conducting properties, which provide for the required cohesion of moist material both in molding and in drying.

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